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Slávka ĽALÍKOVÁ, Mariana PAJTÁŠOVÁ, Darina ONDRUŠOVÁ, Tatiana BAZYLÁKOVÁ, Milan OLŠOVSKÝ, Veronika PETRÁŠOVÁ

STUDY OF POLYMER COMPOUNDS WITH USING OF MONTMORILLONITE FILLER

STUDIUM POLYMERŮ S MONTMORILLONITOVÝM PLNIVEM

[1] ***Department of Inorganic Materials and Environmental Engineering, Faculty of Industrial Technologies, University of Trenčín, 02001 Púchov, Slovakia, e-mail:lalikova@fpt.tnuni.sk***

Abstract

The present work studies a one of the possible applications of inorganic substances, specifically of natural clays and their use in rubber technology. In a function of reinforcement filler at the preparation of modified polymer compounds was used a natural form of bentonite, which was submitted to measurements of thermal (DTA, TG, DSC) and spectral (IR) methods. The influence of type and quantity of the used filler was evaluated by a determination of cure characteristics and physical-mechanical properties at the final vulcanizates. The measured values were compared with the values of commercially used polymer materials with the original composition.

Key words: bentonite, montmorillonite, fillers, physical-mechanical properties, cure characteristics

1. Introduction

Polymer nanocomposites, which represent a new alternative of conventionally filled polymers, are recognized as one of the most promising research areas in polymer science and technology in the 21. century [1]. Polymer nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These improvements at the polymer nanocomposites are connected with the aspect ratio of fillers, their degree of dispersion and orientation in the matrix, and with the adhesion of the fillers to the matrix interface [2]. The most common nano-sized fillers are carbon nanotubes, nanosized particles and intercalated layers [3].The contents of fillers on the basis of layered silicates are relatively low in the range 2 - 6 wt. %, what is a big positive in compare with a high degree of filling, which is typical for conventional used fillers [4]. Besides increased modulus and strength, other factors such as tear properties, fracture toughness and abrasion resistance are claimed to be improved as a result of clay addition to rubber [5-7]. While clay nanocomposites have been investigated in combination with many thermoplastics and thermosetting polymers, much less attention has been paid to the elastomers as matrices [8-11].

2. Experimental

Materials

Natural rubber of type SMR-20, which was used as the elastomeric matrix was obtained from Malaysia. The natural bentonite, which was used in a function of reinforcement filler is a commercial product of Slovak firm Envigeo, a. s., specifically from deposit in the area of Lieskovec. The size of particles of this bentonite product was less than 0,045 mm. Carbon black of type N660 was used as the conventional filler. The others ingredients and their used amounts are mentioned in Table 1. All agents were used directly without any further purification and modification.

Characterization of clay

The detailed characterization of used filler, natural bentonite was obtained by measurements of thermal (DTA, TG, DSC) and spectral (FTIR) analysis. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were simultaneously carried out on a Derivatograph-MOM, Hungary. The weight of the sample was 150 mg. The sample was heated at a heating rate of 10 °C/min from 25 to 900 °C in a nitrogen atmosphere.

For study of differential scanning calorimetry (DSC) was used a calorimeter PYRIS Diamond DSC Perkin Elmer. The thermal scan was performed from 30 °C to 250 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Infrared (IR) spectra were obtained with using KBr pellets on a MB AUXILIARY SAMPLE COMPT. FTIR spectrometer in the middle region (4000 - 400 cm^{-1}).

Preparation of modified rubber compounds

Modified rubber compounds were prepared as follows: The natural rubber of type SMR-20 with montmorillonite filler and all others vulcanization ingredients except the sulphur N were mixed in mixing chamber of laboratory mixer Plastograf-Brabender at 140 °C for 8 min at the mixing speed 50 rpm. The second step, when was added the sulphur N was made at 110 °C for 6 min at the same mixing speed [12]. The composition of the modified rubber compounds is given in Table 1 [13].

Table 1 The composition of prepared modified rubber mixtures

Compounds	Reference compound [phr]	Modified compound 1 [phr]	Modified compound 2 [phr]
SMR-20		100	
ZnO	4,6	4,6	4,6
Sulfenax CBS*	1,5	1,5	1,5
Carbon black N660	10	5	-
Bentonite	-	5	10
Sulphur N		1,8	

*N-cyclohexyl-2-benzothiazolsulfenamid

The slabs were obtained by a compression moulding of the prepared modified rubber compounds using a laboratory press Buzuluk at 150 °C for optimum vulcanization time determined as t_{90} by rheometry. The specimens with a shape of double-ended spatulas were mechanically cut out from the vulcanized slabs [12] and were used to measurements of cure characteristics and physical-mechanical properties.

Characterization of modified rubber compounds

The prepared modified rubber compounds were studied by determination of cure characteristics and physical-mechanical properties at final vulcanizates. The curing behavior (M_L, M_H, t_s, t_{90}, R_v) was investigated by using of vulcameter Monsanto 100 at the temperature 150 °C during 60 min [14]. Physical-mechanical properties (tensile strength, modulus at 300 elongation - M_{300}, tensibility) were measured at room temperature by using of instrument Instron at deformation rate 50 mm/min [15]. Hardness was determined at the same temperature by hardness tester IRHD. Four determinations of hardness at three different positions on the specimen were taken and averaged [16].

3. Results and discussion

Characterization of natural bentonite

The thermoanalytical record of natural bentonite from locality Lieskovec is mentioned in Fig. 1. The DTA curve is possible to divide on two areas, the area of dehydration in the thermal interval 20-300 °C and the area of dehydroxylation in the thermal interval 500-1000 °C. The physical bounded molecular water got away by heating at temperatures up to 100-120 °C and the water in interlayers space from 120 °C. The OH groups began to release at the temperature around 500 °C and the dehydroxylation finished up to 800 °C.

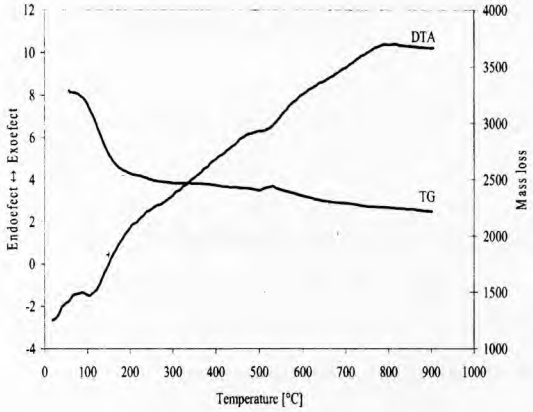

Fig. 1 DTA and TG of natural bentonite

The first endothermic peak on the DSC curve (Fig. 2) is assigned to the loss of adsorbed water residing between bentonite crystallites. For natural bentonite release of water begins around 40 °C, and continues till about 120 °C. and the water in interlayers space from 120 °C. Between 400 and 700°C, dehydroxylation of the aluminosilicate occurs.

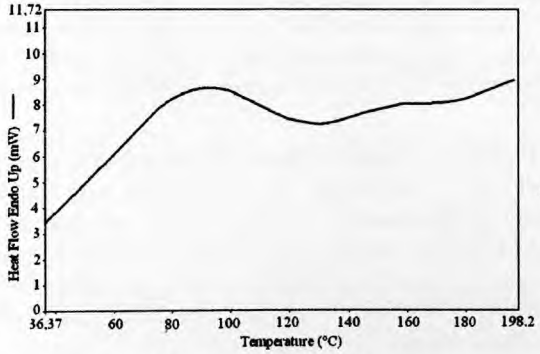

Fig. 2 DSC of natural bentonite

Infrared spectra provide information on the minerals present in the sample and on the chemical composition of the dominant minerals. Fig. 3 shows the FTIR spectra of the untreated sample in the wavenumber range 4000 - 400 cm^{-1}. The band at 3618 cm^{-1} is result the –OH stretching vibration of the structural OH groups in bentonite. The broad bands at 3420 cm^{-1} and 1629 cm^{-1} are characteristic of the stretching and bending vibrations of sorbed water. The strong absorption band at 1018 cm^{-1} is

result of Si–O stretching vibrations. The bands near 908 and 783 cm^{-1}, respectively, correspond to vibrational frequencies of Al-Al-OH and Mg-Fe-OH. A peak at 682 cm^{-1} was due to the bending vibration of Si-O-Si. Tetrahedral bending modes were observed for Si-O-Al at 516 cm^{-1}.

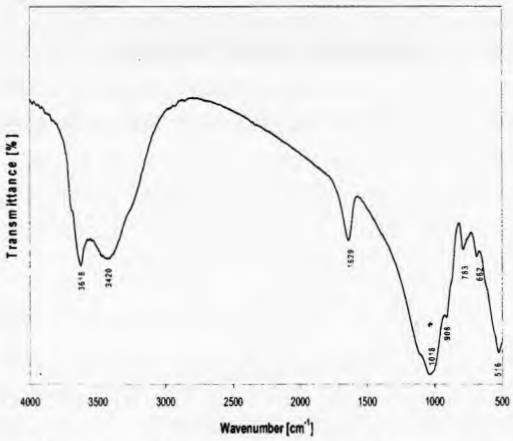

Fig. 3 The IR spectra of natural bentonite

Characterization of modified rubber compounds

The results of measured cure characteristics (M_L, M_H, t_s, t_{90}, R_V) of prepared modified rubber compounds are present in Table 2.

Table 2 Cure characteristics of prepared modified rubber compounds

	Measure	Reference compound	Modified compound 1	Modified compound 2
M_L	N.m	5,0	2,7	1,8
M_H	N.m	45,0	43,8	38,5
t_s	min	1,5	1,5	4
t_{90}	min	3,5	4,6	8,2
R_V	min^{-1}	50,00	32,26	23,81

From the obtained values in Table 2 follow, that the selected type of filler acts as an inactive filler in prepared modified rubber compounds. We can see, that with an increasing amount of natural bentonite in modified compounds a viscosity decrease (lower values of M_L and M_H) and the optimal time of vulcanization (t_{90}) extend. At the modified rubber compound 2, where is a total substitution of carbon black is more than 100 % and the scorch of time (t_s) is expressively higher too (Fig. 4). The values of rate coefficients of vulcanization (R_V), which characterize „activity" of ingredients in modified rubber compounds are markedly lower too.

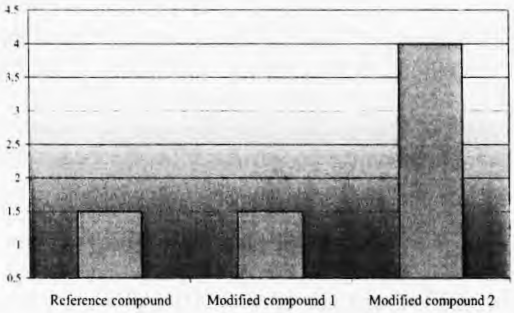

Fig. 4 Scorch of time

The results of measured physical and mechanical properties of prepared modified rubber compounds are present in Table 3.

Table 3 Physical - mechanical properties of prepared modified rubber compounds

Type of test	Measure	Reference compound	Modified compound 1	Modified compound 2
Tensile strength	MPa	13,17	14,90	20,10
Modulus 300	MPa	5,77	8,29	7,58
Tensibility	%	685	539	796
Hardness	IRHD	47,6	46,2	43,3

The measured and evaluated values of physical-mechanical parameters show, that tensile strength increases with an increasing content of natural bentonite in tested modified rubber compounds. At 100 % substitution of carbon black N660 is the tensile strenght higher about more than 50 % (Fig.5). On the other hand, the tensibility decreases with an increasing amount of natural bentonite in modified rubber compound, what is logical and confirms of the elastomeric behaviour of modified rubber compound [17,18]. The values of hardness decrease with an increasing content of natural bentonite what relate with a less „activity" of natural bentonite in compare with the carbon black N660 and so with a less interaction of polymer-filler [17,18]. But this decrease of hardness values isn't very dramatic.

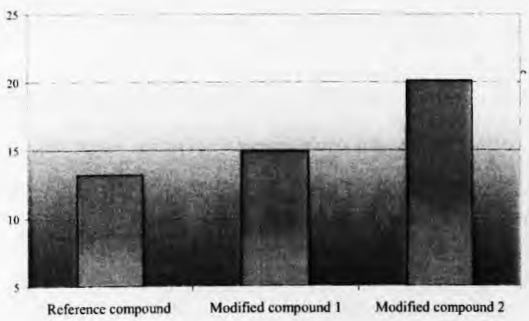

Fig. 5 Tensile strength

4. Conclusion

The results of measurements of IR, DTA, TG and DSC at the investigated filler confirmed of values, which are typical for natural bentonite with a high content of clay mineral, montmorillonite. From present study follow too, that addition of filler on the base of natural clay, bentonite has a positive effect on physical - mechanical properties of final vulcanizates.

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Reviewer: Doc. Ing. Petr Pánek, CSc., VŠB – TU Ostrava